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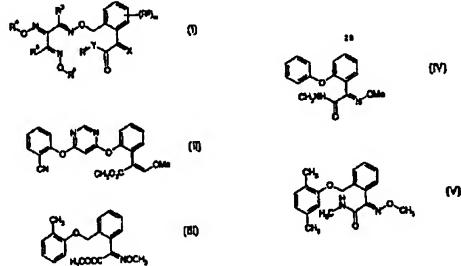
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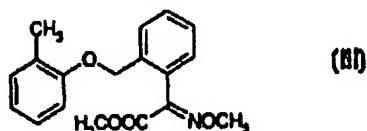
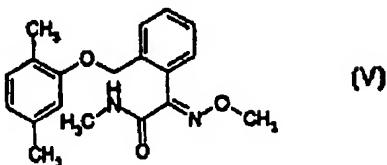
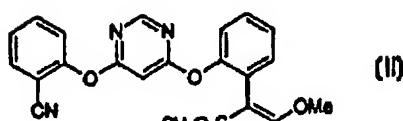
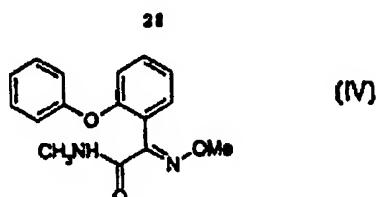
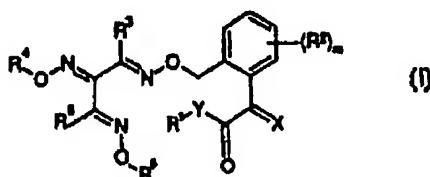
(54) MELANGES FONGICIDES A BASE DE DERIVES D'OXIMETHER DE DIATOMITE ET D'AUTRES STROBILURINES  
(54) FUNGICIDE MIXTURES BASED ON TRIPLE OXIME ETHER DERIVATIVES AND OTHER STROBILURINS

(57) The invention relates to fungicide mixtures comprised as active components a) phenylacetic acid derivatives of formula (I) in which the substituents and the index have the meanings cited in the description, and the salts thereof, and b) at least one compound of formulas (II) to (V) in a synergistically effective quantity.



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(30) 1998/03/24 (19812764.2) DE  
(54) **MELANGES FONGICIDES A BASE DE DERIVATIVES  
D'OXIMETHER DE DIATOMITE ET D'AUTRES  
STROBILURINES**  
(54) **FUNGICIDE MIXTURES BASED ON TRIPLE CHARGE  
DERIVATIVES AND OTHER STROBILURINES**



(57) L'invention concerne des mélanges fongicides contenant comme constituants actifs (a) des dérivés d'acide phényleacétique de la formule (I), dans laquelle les substituants et l'indice ont la signification indiquée dans la description, ainsi que leurs sels, et (b) au moins un composé des formules (II) à (V) dans des quantités produisant un effet synergique.

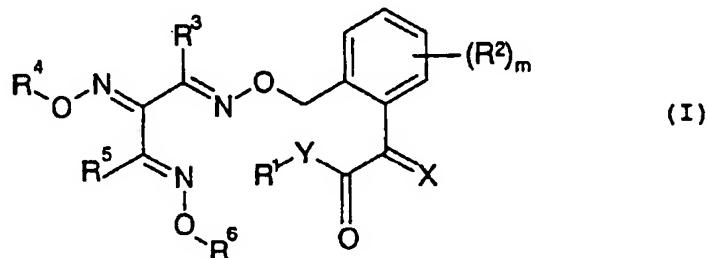
(57) The invention relates to fungicide mixtures comprised as active components a) phenylacetic acid derivatives of formula (I) in which the substituents and the index have the meanings cited in the description, and the salts thereof, and b) at least one compound of formulas (II) to (V) in a synergistically effective quantity.

FUNGICIDE MIXTURES BASED ON TRIPLE OXIME ETHER  
DERIVATIVES AND OTHER STROBILURINS

The present invention relates to fungicidal mixtures for controlling harmful fungi which [lacuna]

a) phenylacetic acid derivatives of the formula I

10



in which the substituents and the index have the following meaning:

20

X is  $\text{NOCH}_3$ ,  $\text{CHOCH}_3$ ,  $\text{CHCH}_3$ ;

Y is O, NR

$\text{R}^1$ , R independently of one another are each hydrogen and  $\text{C}_1\text{-C}_4$ -alkyl;

$\text{R}^2$  is cyano, nitro, trifluoromethyl, halogen,  $\text{C}_1\text{-C}_4$ -alkyl and  $\text{C}_1\text{-C}_4$ -alkoxy;

$\text{m}$  is 0, 1 or 2, where the radicals  $\text{R}^2$  may be different if  $\text{m}$  is 2;

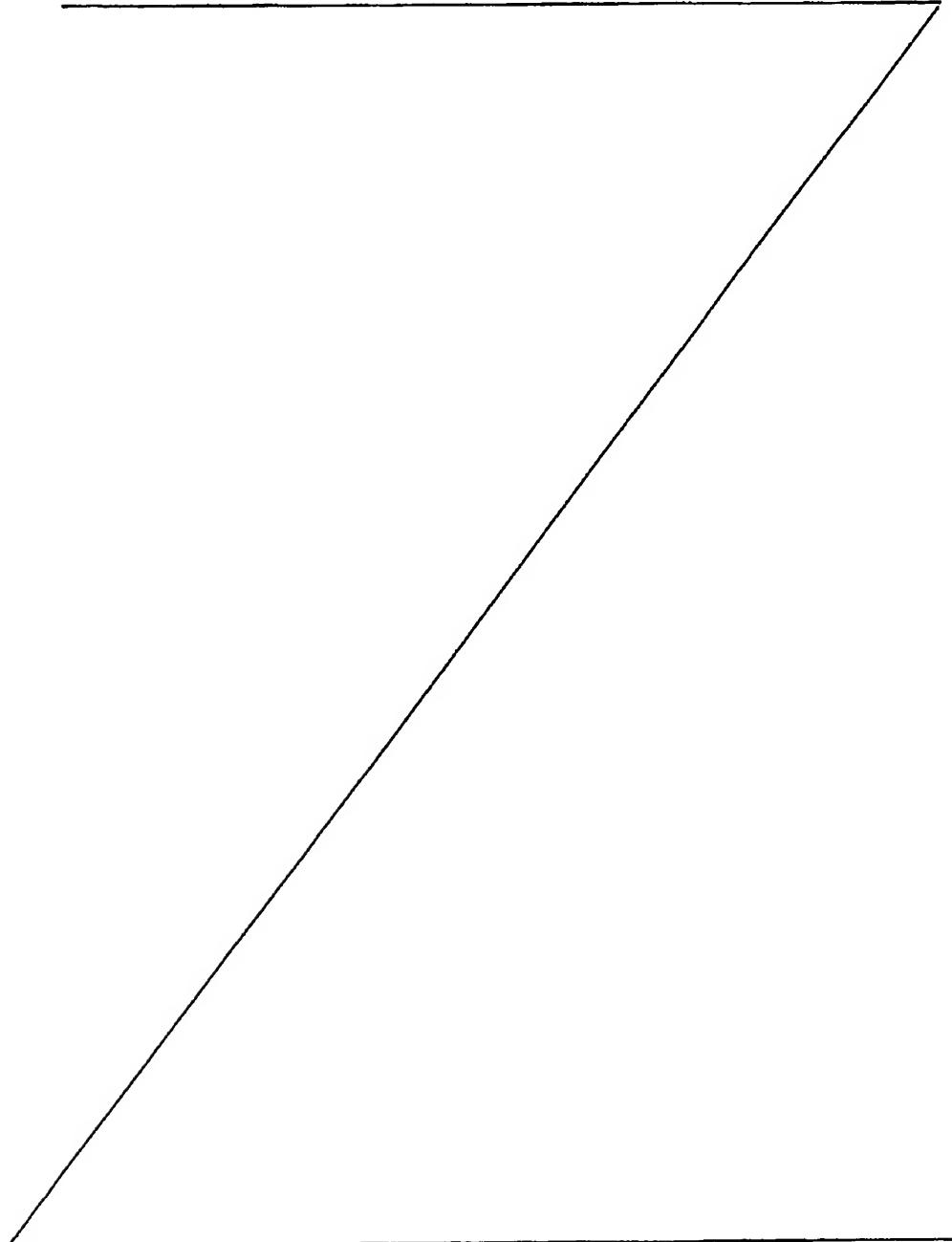
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$\text{R}^3$  is hydrogen, cyano,  $\text{C}_1\text{-C}_4$ -alkyl,  $\text{C}_1\text{-C}_4$ -haloalkyl,  $\text{C}_3\text{-C}_6$ -cycloalkyl;

1a

$R^4$ ,  $R^6$  independently of one another are each hydrogen,

are  $C_1$ - $C_{10}$ -alkyl,  $C_3$ - $C_6$ -cycloalkyl,  $C_2$ - $C_{10}$ -alkenyl,  
 $C_2$ - $C_{10}$ -alkynyl,  $C_1$ - $C_{10}$ -alkylcarbonyl,  
 $C_2$ - $C_{10}$ -alkenylcarbonyl,  $C_3$ - $C_{10}$ -alkynylcarbonyl or



$C_1-C_{10}$ -alkylsulfonyl, where these radicals may be partially or fully halogenated or may carry one to three of the following groups: cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocarbonyl, halogen,  $C_1-C_6$ -alkyl,  $C_1-C_6$ -haloalkyl,  $C_1-C_6$ -alkylsulfonyl,  $C_1-C_6$ -alkylsulfoxy,  $C_1-C_6$ -haloalkoxy,  $C_1-C_6$ -alkoxycarbonyl,  $C_1-C_6$ -alkylthio,  $C_1-C_6$ -alkylamino, di- $C_1-C_6$ -alkylamino,  $C_1-C_6$ -alkylaminocarbonyl, di- $C_1-C_6$ -alkylaminocarbonyl,  $C_1-C_6$ -alkylaminothiocarbonyl, di- $C_1-C_6$ -alkylaminothiocarbonyl,  $C_2-C_6$ -alkenyl,  $C_2-C_6$ -alkenyloxy,  $C_3-C_6$ -cycloalkyl,  $C_3-C_6$ -cycloalkyloxy, heterocyclyl, heterocyclxy, benzyl, benzyloxy, aryl, aryloxy, arylthio, hetaryl, hetaryloxy and hetarylthio, where the cyclic groups for their part may be partially or fully halogenated or may carry one to three of the following groups: cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocarbonyl, halogen,  $C_1-C_6$ -alkyl,  $C_1-C_6$ -haloalkyl,  $C_1-C_6$ -alkylsulfonyl,  $C_1-C_6$ -alkylsulfoxy,  $C_3-C_6$ -cycloalkyl,  $C_1-C_6$ -alkoxy,  $C_1-C_6$ -haloalkoxy,  $C_1-C_6$ -alkyloxycarbonyl,  $C_1-C_6$ -alkylthio,  $C_1-C_6$ -alkylamino, di- $C_1-C_6$ -alkylamino,  $C_1-C_6$ -alkylaminocarbonyl, di- $C_1-C_6$ -alkylaminocarbonyl,  $C_1-C_6$ -alkylaminothiocarbonyl, di- $C_1-C_6$ -alkylaminothiocarbonyl,  $C_2-C_6$ -alkenyl,  $C_2-C_6$ -alkenyloxy, benzyl, benzyloxy, aryl, aryloxy, arylthio, hetaryl, hetaryloxy, hetarylthio or  $C(=NOR^7)-A_n-R^8$ ;

are aryl, arylcarbonyl, arylsulfonyl, hetaryl, hetarylcarbonyl or hetaryl sulfonyl, where these radicals may be partially or fully halogenated or may carry one to three of the following groups: cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocarbonyl, halogen,  $C_1-C_6$ -alkyl,  $C_1-C_6$ -haloalkyl,  $C_1-C_6$ -alkylcarbonyl,  $C_1-C_6$ -alkylsulfonyl,  $C_1-C_6$ -alkylsulfoxy,  $C_3-C_6$ -cycloalkyl,  $C_1-C_6$ -alkoxy,  $C_1-C_6$ -haloalkoxy,  $C_1-C_6$ -alkyloxycarbonyl,  $C_1-C_6$ -alkylthio,  $C_1-C_6$ -alkylamino, di- $C_1-C_6$ -alkylamino,  $C_1-C_6$ -alkylaminocarbonyl, di- $C_1-C_6$ -alkylaminocarbonyl,  $C_1-C_6$ -alkylaminothiocarbonyl, di- $C_1-C_6$ -alkylaminothiocarbonyl,  $C_2-C_6$ -alkenyl,  $C_2-C_6$ -alkenyloxy, benzyl, benzyloxy, aryl, aryloxy, hetaryl, hetaryloxy or  $C(=NOR^7)-A_n-R^8$ ;

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$R^5$  is hydrogen,

5 is  $C_1$ - $C_6$ -alkyl,  $C_2$ - $C_6$ -alkenyl,  $C_2$ - $C_6$ -alkynyl, where the hydrocarbon radicals of these groups may be partially or fully halogenated or may carry one to three of the following radicals: cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocarbonyl, halogen,  $C_1$ - $C_6$ -alkylaminocarbonyl,  $di-C_1$ - $C_6$ -alkylaminocarbonyl,  $C_1$ - $C_6$ -alkylaminothiocarbonyl,  $di-C_1$ - $C_6$ -alkylaminothiocarbonyl,  $C_1$ - $C_6$ -alkylsulfonyl,  $C_1$ - $C_6$ -alkylsulfoxyl,  $C_1$ - $C_6$ -alkoxy,  $C_1$ - $C_6$ -haloalkoxy,  $C_1$ - $C_6$ -alkoxycarbonyl,  $C_1$ - $C_6$ -alkylthio,  $C_1$ - $C_6$ -alkylamino,  $di-C_1$ - $C_6$ -alkylamino,  $C_2$ - $C_6$ -alkenyloxy,  $C_3$ - $C_6$ -cycloalkyl,  $C_3$ - $C_6$ -cycloalkyloxy, heterocyclyl, heterocyclyloxy, aryl, aryloxy, aryl- $C_1$ - $C_4$ -alkoxy, arylthio, aryl- $C_1$ - $C_4$ -alkylthio, hetaryl, hetaryloxy, hetaryl- $C_1$ - $C_4$ -alkoxy, hetarylthio, hetaryl- $C_1$ - $C_4$ -alkylthio, where the cyclic radicals for their part may be partially or fully halogenated and/or may carry one to three of the following groups: cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocarbonyl,  $C_1$ - $C_6$ -alkyl,  $C_1$ - $C_6$ -haloalkyl,  $C_1$ - $C_6$ -alkylsulfonyl,  $C_1$ - $C_6$ -alkylsulfoxyl,  $C_3$ - $C_6$ -cycloalkyl [sic],  $C_1$ - $C_6$ -alkoxy,  $C_1$ - $C_6$ -haloalkoxy,  $C_1$ - $C_6$ -alkoxycarbonyl,  $C_1$ - $C_6$ -alkylthio,  $C_1$ - $C_6$ -alkylamino,  $di-C_1$ - $C_6$ -alkylamino,  $C_1$ - $C_6$ -alkylaminocarbonyl,  $di-C_1$ - $C_6$ -alkylaminocarbonyl,  $C_1$ - $C_6$ -alkylaminothiocarbonyl,  $di-C_1$ - $C_6$ -alkylaminothiocarbonyl,  $C_2$ - $C_6$ -alkenyl,  $C_2$ - $C_6$ -alkenyloxy, benzyl, benzyloxy, aryl, aryloxy, arylthio, hetaryl, hetaryloxy, hetarylthio and  $C(=NOR^7)-A_n-R^8$ ;

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$C_2$ - $C_6$ -alkenyloxy, benzyl, benzyloxy, aryl, aryloxy,  
hetaryl and hetaryloxy;

where

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A is oxygen, sulfur or nitrogen and where the nitrogen carries hydrogen or  $C_1$ - $C_6$ -alkyl;

10

n is 0 or 1;

$R^7$  is hydrogen or  $C_1$ - $C_6$ -alkyl and

15

$R^8$  is hydrogen or  $C_1$ - $C_6$ -alkyl,

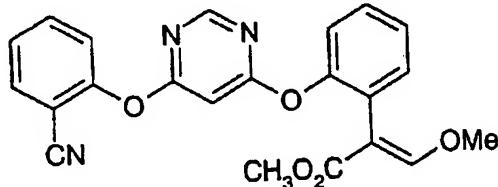
and their salts,

and

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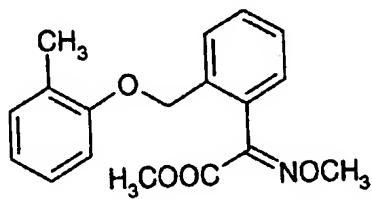
b) at least one fungicide selected from the fungicides of the formulae II to V

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(II)

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(III)

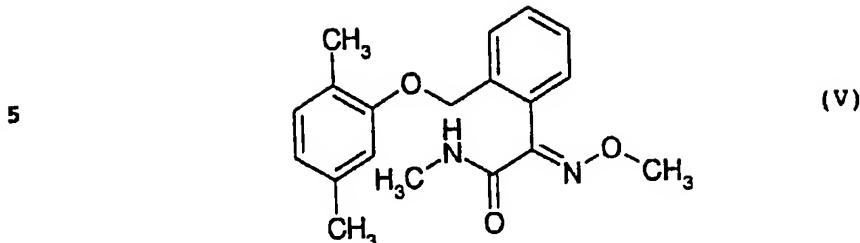
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(IV)

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It is an object of the present invention to provide fungicidal mixtures which have good fungicidal activity exceeding the activity of the mixture components on their own, in particular 15 against fungal diseases in rice.

We have found that this object is achieved by the mixtures as claimed in claim 1.

20 The compounds of the formula I are known per se and are described in the literature (WO 97/15552).

25 The fungicides of the formulae II to V are also known and described in the literature. In addition, they may, if appropriate, be commercially available under the trade names mentioned below in brackets:

30 II: common name: azoxystrobin (trade name: Amistar®, from Zeneca)

III: EP- A 253,313, common name: kresoxim-methyl (trade name Brio®, from BASF)

35 IV: EP 398,692, proposed common name: metominostrobin (development code SSF-126, from Shionogi);

40 V: EP 398,692, CAS RN 162535-21-9, SSF 129, development product of Shionogi Co., Ltd.)

Owing to their C=C and C=N double bonds, the preparation of the compounds I may yield E/Z isomer mixtures which can be separated into the individual compounds in a customary manner, for example 45 by crystallization or chromatography.

However, if the synthesis yields isomer mixtures, a separation is generally not necessarily required since in some cases the individual isomers can be converted into one another during the preparation for use or upon use (for example under the action of 5 light, acids or bases). Similar conversions may also occur after use, for example in the treatment of plants in the treated plant or in the harmful fungus or animal pest to be controlled.

With regard to the C=X double bond, preference is given to the E 10 isomers of the compounds I (configuration based on the -OCH<sub>3</sub> or the -CH<sub>3</sub> group in relation to the -CO<sub>2</sub>R<sup>1</sup> group) with respect to their activity.

15 With regard to the -C(R<sup>3</sup>)=NOCH<sub>2</sub>- double bond, preference is given to the cis isomers of the compounds I (configuration based on the radical R<sup>3</sup> in relation to the -OCH<sub>2</sub>- group) with respect to their activity.

20 In the definitions of the compounds I given at the outset, collective terms were used which generally represent the following groups:

Halogen: fluorine, chlorine, bromine and iodine;

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Alkyl: straight-chain or branched alkyl groups having 1 to 4, 6 or 10 carbon atoms, for example C<sub>1</sub>-C<sub>6</sub>-alkyl such as methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, pentyl, 1-methylbutyl, 2-methylbutyl,

30 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, hexyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 35 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methylpropyl and 1-ethyl-2-methylpropyl;

40 Haloalkyl: straight-chain or branched alkyl groups having 1 to 6 carbon atoms, it being possible for some or all of the hydrogen atoms in these groups to be replaced by halogen atoms as mentioned above, for example C<sub>1</sub>-C<sub>2</sub>-haloalkyl, such as chloromethyl, dichloromethyl, trichloromethyl, fluoromethyl, difluoromethyl, trifluoromethyl, chlorofluoromethyl,

45 dichlorofluoromethyl, chlorodifluoromethyl, 1-fluoroethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 2-chloro-2-fluoroethyl, 2-chloro-2,2-difluoroethyl,

2,2-dichloro-2-fluoroethyl, 2,2,2-trichloroethyl and pentafluoroethyl;

5 Cycloalkyl: monocyclic alkyl groups having 3 to 6 carbon ring members, for example cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl;

10 Alkenyl: straight-chain or branched alkenyl groups having 2 to 6 or 10 carbon atoms and a double bond in any position, for example C<sub>2</sub>-C<sub>6</sub>-alkenyl, such as ethenyl, 1-propenyl, 2-propenyl, 1-methylethenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 2-methyl-1-propenyl, 1-methyl-2-propenyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1-methyl-1-butenyl, 2-methyl-1-butenyl, 3-methyl-1-butenyl, 1-methyl-2-butenyl, 2-methyl-2-butenyl, 3-methyl-2-butenyl, 1-methyl-3-butenyl, 2-methyl-3-butenyl, 3-methyl-3-butenyl, 1,1-dimethyl-2-propenyl, 1,2-dimethyl-1-propenyl, 1,2-dimethyl-2-propenyl, 1-hexenyl, 2-hexenyl, 1-ethyl-1-propenyl, 1-ethyl-2-propenyl, 3-hexenyl, 4-hexenyl, 5-hexenyl, 1-methyl-1-pentenyl, 2-methyl-1-pentenyl, 3-methyl-1-pentenyl, 4-methyl-1-pentenyl, 1-methyl-2-pentenyl, 2-methyl-2-pentenyl, 3-methyl-2-pentenyl, 4-methyl-2-pentenyl, 1-methyl-3-pentenyl, 2-methyl-3-pentenyl, 3-methyl-3-pentenyl, 4-methyl-3-pentenyl, 1-methyl-4-pentenyl, 2-methyl-4-pentenyl, 3-methyl-4-pentenyl, 4-methyl-4-pentenyl, 1,1-dimethyl-2-butenyl, 1,1-dimethyl-3-butenyl, 1,2-dimethyl-1-butenyl, 1,2-dimethyl-2-butenyl, 1,2-dimethyl-3-butenyl, 1,3-dimethyl-1-butenyl, 1,3-dimethyl-2-butenyl, 1,3-dimethyl-3-butenyl, 2,2-dimethyl-3-butenyl, 2,3-dimethyl-1-butenyl, 2,3-dimethyl-2-butenyl, 3,3-dimethyl-1-butenyl, 3,3-dimethyl-2-butenyl, 1-ethyl-1-butenyl, 1-ethyl-2-butenyl, 1-ethyl-3-butenyl, 2-ethyl-1-butenyl, 2-ethyl-2-butenyl, 2-ethyl-3-butenyl, 1,1,2-trimethyl-2-propenyl, 1-ethyl-1-methyl-2-propenyl, 1-ethyl-2-methyl-1-propenyl and 1-ethyl-2-methyl-2-propenyl;

40 Alkynyl: straight-chain or branched alkynyl groups having 2 to 10 carbon atoms and a triple bond in any position, for example C<sub>2</sub>-C<sub>6</sub>-alkynyl, such as ethynyl, 2-propynyl, 2-butynyl, 3-butynyl, 1-methyl-2-propynyl, 2-pentynyl, 3-pentynyl, 4-pentynyl, 1-methyl-2-butynyl, 1-methyl-3-butynyl, 2-methyl-3-butynyl, 1,1-dimethyl-2-propynyl, 1-ethyl-2-propynyl, 2-hexynyl, 3-hexynyl, 4-hexynyl, 5-hexynyl, 1-methyl-2-pentynyl, 1-methyl-3-pentynyl, 1-methyl-4-pentynyl, 2-methyl-3-pentynyl, 2-methyl-4-pentynyl, 3-methyl-4-pentynyl, 4-methyl-2-pentynyl,

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1,1-dimethyl-2-butynyl, 1,1-dimethyl-3-butynyl,  
 1,2-dimethyl-3-butynyl, 2,2-dimethyl-3-butynyl,  
 1-ethyl-2-butynyl, 1-ethyl-3-butynyl, 2-ethyl-3-butynyl and  
 1-ethyl-1-methyl-2-propynyl;

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Heterocyclyl or heterocycloloxy, heterocyclylthio and  
 heterocyclylamino: three- to six-membered saturated or partially  
 unsaturated mono- or polycyclic heterocycles which contain one to  
 three heteroatoms [sic] selected from a group consisting of  
 10 oxygen, nitrogen and sulfur and which are attached to the  
 skeleton directly or (heterocycloloxy) via an oxygen atom or  
 (heterocyclylthio) via a sulfur atom or (heterocyclylamino) via a  
 nitrogen atom, such as, for example, 2-tetrahydrofuranyl,  
 oxiranyl, 3-tetrahydrofuranyl, 2-tetrahydrothienyl,  
 15 3-tetrahydrothienyl, 2-pyrrolidinyl, 3-pyrrolidinyl,  
 3-isoxazolidinyl, 4-isoxazolidinyl, 5-isoxazolidinyl,  
 3-isothiazolidinyl, 4-isothiazolidinyl, 5-isothiazolidinyl,  
 3-pyrazolidinyl, 4-pyrazolidinyl, 5-pyrazolidinyl,  
 20 2-oxazolidinyl, 4-oxazolidinyl, 5-oxazolidinyl, 2-thiazolidinyl,  
 4-thiazolidinyl, 5-thiazolidinyl, 2-imidazolidinyl,  
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 1,2,4-oxadiazolidin-5-yl, 1,2,4-thiadiazolidin-3-yl,  
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 1,3,4-oxadiazolidin-2-yl, 1,3,4-thiadiazolidin-2-yl,  
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 2,5-dihydrothiazol-4-yl, 2,5-dihydrothiazol-5-yl,  
 2,3-dihydroimidazol-2-yl, 2,3-dihydroimidazol-4-yl,  
 5 2,3-dihydroimidazol-5-yl, 4,5-dihydroimidazol-2-yl,  
 4,5-dihydroimidazol-4-yl, 4,5-dihydro-imidazol-5-yl,  
 2,5-dihydroimidazol-2-yl, 2,5-dihydroimidazol-4-yl,  
 2,5-dihydroimidazol-5-yl, 2-morpholinyl, 3-morpholinyl,  
 2-piperidinyl, 3-piperidinyl, 4-piperidinyl,  
 10 3-tetrahydropyridazinyl, 4-tetrahydropyridazinyl,  
 2-tetrahydropyrimidinyl, 4-tetrahydropyrimidinyl,  
 5-tetrahydropyrimidinyl, 2-tetrahydropyrazinyl,  
 1,3,5-tetrahydrotriazin-2-yl, 1,2,4-tetrahydrotriazin-3-yl,  
 1,3-dihydrooxazin-2-yl, 1,3-dithian-2-yl, 2-tetrahydropyranyl,  
 15 1,3-dioxolan-2-yl, 3,4,5,6-tetrahydropyridin-2-yl,  
 4H-1,3-thiazin-2-yl, 4H-3,1-benzothiazin-2-yl,  
 1,1-dioxo-2,3,4,5-tetrahydrothien-2-yl, 2H-1,4-benzothiazin-3-yl,  
 2H-1,4-benzoxazin-3-yl, 1,3-dihydrooxazin-2-yl, 1,3-dithian-2-yl;  
 20 20 Aryl or aryloxy, arylthio, arylcarbonyl and arylsulfonyl:  
 aromatic mono- or polycyclic hydrogen radicals which are attached  
 to the skeleton directly or (aryloxy) via an oxygen atom (-O-) or  
 (arylthio) a sulfur atom (-S-), (arylcarbonyl) via a carbonyl  
 group (-CO-) or (arylsulfonyl) via a sulfonyl group (-SO<sub>2</sub>-), for  
 25 example phenyl, naphthyl and phenanthrenyl or phenyloxy,  
 naphthyoxy and phenanthrenyloxy and the corresponding carbonyl  
 and sulfonyl radicals;  
 30 30 Hetaryl or hetaryloxy, hetarylthio, hetarylcarbonyl and  
 hetarylsulfonyl: aromatic mono- or polycyclic radicals which,  
 beside carbon ring members, can additionally contain one to four  
 nitrogen atoms or one to three nitrogen atoms and one oxygen or  
 one sulfur atom or one oxygen or one sulfur atom and which are  
 attached to the skeleton directly or (hetaryloxy) via an oxygen  
 35 atom (-O-) or (hetarylthio) a sulfur atom (-S-),  
 (hetarylcarbonyl) via a carbonyl group (-CO-) or  
 (hetarylsulfonyl) via a sulfonyl group (-SO<sub>2</sub>-), for example  
 40 - 40 - 5-membered heteroaryl, containing one to three nitrogen  
 atoms: 5-membered heteroaryl groups which, beside carbon  
 atoms, can contain one to three nitrogen atoms as ring  
 members, for example 2-pyrrolyl, 3-pyrrolyl, 3-pyrazolyl,  
 4-pyrazolyl, 5-pyrazolyl, 2-imidazolyl, 4-imidazolyl,  
 45 1,2,4-triazol-3-yl and 1,3,4-triazol-2-yl;

## 10

- 5-membered heteroaryl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom or one oxygen or one sulfur atom: 5-membered heteroaryl groups which, beside carbon atoms, can contain one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom or one oxygen or sulfur atom as ring members, for example 2-furyl, 3-furyl, 2-thienyl, 3-thienyl, 5-pyrrolyl, 3-pyrrolyl, 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, 3-isothiazolyl, 4-isothiazolyl, 5-isothiazolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-imidazolyl, 4-imidazolyl, 1,2,4-oxadiazol-3-yl, 1,2,4-oxadiazol-5-yl, 1,2,4-thiadiazol-3-yl, 1,2,4-thiadiazol-5-yl, 15 1,2,4-triazol-3-yl, 1,3,4-oxadiazol-2-yl, 1,3,4-thiadiazol-2-yl, 1,3,4-triazol-2-yl;
- benzo-fused 5-membered heteroaryl, containing one to three nitrogen atoms or one nitrogen atom and/or one oxygen or sulfur atom: 5-membered heteroaryl groups which, beside carbon atoms, can contain one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom or one oxygen or one sulfur atom as ring members, and in which two adjacent carbon ring members or one nitrogen and one adjacent carbon ring member may be bridged by a buta-1,3-dien-1,4-diyl group;
- 5-membered heteroaryl bonded via nitrogen and containing one to four nitrogen atoms, or benzo-fused 5-membered heteroaryl, bonded via nitrogen and containing one to three nitrogen atoms: 5-membered heteroaryl groups which, beside carbon atoms, can contain one to four nitrogen atoms and one to three nitrogen atoms, respectively, as ring members, and in which two adjacent carbon ring members or one nitrogen and one adjacent carbon ring member can be bridged by a buta-1,3-dien-1,4-diyl group, these rings being attached to the skeleton via one of the nitrogen ring members;
- 40 - 6-membered heteroaryl containing one to three and one to four nitrogen atoms, respectively: 6-membered heteroaryl groups which, beside carbon atoms, can contain one to three nitrogen atoms and one to four nitrogen atoms, respectively, as ring members, for example 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, 3-pyridazinyl, 4-pyridazinyl, 2-pyrimidinyl, 4-pyrimidinyl, 45 5-pyrimidinyl, 2-pyrazinyl, 1,3,5-triazin-2-yl,

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1,2,4-triazin-3-yl and 1,2,4,5-tetrazin-3-yl;

5 - benzo-fused 6-membered heteroaryl containing one to four nitrogen atoms: 6-membered heteroaryl groups in which two adjacent carbon ring members can be bridged by a buta-1,3-dien-1,4-diyl group, for example quinoline, isoquinoline, quinazoline and quinoxaline,

10 and the corresponding oxy, thio, carbonyl or sulfonyl groups.

15 Hetarylarnino: aromatic mono- or polycyclic radicals which, beside carbon ring members, can additionally contain one to four nitrogen atoms or one to three nitrogen atoms and one oxygen or one sulfur atom and which are attached to the skeleton via a nitrogen atom.

20 The specification "partially or fully halogenated" is meant to express that some or all of the hydrogen atoms in the groups thus characterized may be replaced by identical or different halogen atoms as mentioned above.

25 With respect to their biological activity, preference is given to compounds of the formula I in which  $m$  is 0.

Likewise, preference is given to compounds of formula I in which  $R^1$  is methyl.

30 Besides, preference is given to compounds I in which  $R^3$  is hydrogen, cyano, cyclopropyl, methyl, ethyl, 1-methylethyl or  $CF_3$ .

Moreover, preference is given to compounds I in which  $R^3$  is methyl.

35 Besides, preference is given to compounds I in which  $R^3$  is cyano.

Furthermore, preference is given to compounds I in which  $R^3$  is cyclopropyl.

40 Additionally, preference is given to compounds I in which  $R^3$  is  $CF_3$ .

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Additionally, preference is given to compounds I in which R<sup>5</sup> is hydrogen, cyclopropyl, methyl, ethyl, isopropyl, unsubstituted or substituted aryl or hetaryl.

5 Moreover, preference is given to compounds I in which R<sup>5</sup> is methyl.

10 Additionally, preference is given to compounds I in which R<sup>5</sup> is ethyl.

15 Moreover, preference is given to compounds I in which R<sup>5</sup> is isopropyl.

20 Moreover, preference is given to compounds I in which R<sup>5</sup> is cyclopropyl.

25 Moreover, preference is given to compounds I in which R<sup>5</sup> is CF<sub>3</sub>.

30 Additionally, preference is given to compounds I in which R<sup>5</sup> is unsubstituted or substituted aryl or hetaryl.

35 Additionally, preference is given to compounds I in which R<sup>5</sup> is unsubstituted or substituted pyridyl, pyrimidyl, pyrazinyl, pyridazinyl or triazinyl.

40 Additionally, preference is given to compounds I in which R<sup>5</sup> is unsubstituted or substituted furyl, thienyl or pyrrolyl.

45 Additionally, preference is given to compounds I in which R<sup>5</sup> is unsubstituted or substituted oxazolyl, thiazolyl, isoxazolyl, isothiazolyl, pyrazolyl or imidazolyl.

50 Additionally, preference is given to compounds I in which R<sup>5</sup> is oxadiazolyl [sic], thiadiazolyl or triazolyl.

55 Moreover, preference is given to compounds I in which R<sup>5</sup> is phenyl which is unsubstituted or carries one or two of the following groups: nitro, cyano, hydroxyl, amino, aminocarbonyl, aminothiocarbonyl, halogen, C<sub>1</sub>-C<sub>4</sub>-alkyl, C<sub>1</sub>-C<sub>4</sub>-haloalkyl, C<sub>1</sub>-C<sub>4</sub>-alkoxy, C<sub>1</sub>-C<sub>4</sub>-haloalkoxy, C<sub>1</sub>-C<sub>4</sub>-alkylamino, di-C<sub>1</sub>-C<sub>4</sub>-alkylamino, C<sub>1</sub>-C<sub>4</sub>-alkylsulfonyl, C<sub>1</sub>-C<sub>4</sub>-alkoxycarbonyl, C<sub>1</sub>-C<sub>4</sub>-alkylaminocarbonyl or di-C<sub>1</sub>-C<sub>4</sub>-alkylaminocarbonyl.

Moreover, preference is given to compounds I in which R<sup>4</sup> is hydrogen, C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>2</sub>-C<sub>6</sub>-alkenyl, C<sub>2</sub>-C<sub>6</sub>-alkynyl, allyl, arylalkyl, hetarylalkyl, aryloxyalkyl, hetarylxyalkyl, aryl or hetaryl.

5

Additionally, preference is given to compounds I in which R<sup>4</sup> is C<sub>1</sub>-C<sub>6</sub>-alkyl.

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Further preferred compounds I are disclosed in WO 97/15,552.

10

The compounds I which are contained in the mixtures according to the invention have excellent activity against a broad range of phytopathogenic fungi, in particular against fungi from the classes of the Ascomycetes, Deuteromycetes, Phycomycetes and Basidiomycetes.

They are especially important for controlling a large number of fungi in a variety of crop plants, such as cotton, vegetable 20 species (for example cucumbers, beans, tomatoes, potatoes and cucurbits), barley, grass, oats, bananas, coffee, maize, fruit species, rice, rye, soya, grapevine, wheat, ornamentals, sugar cane, and a variety of seeds.

25 They are particularly suitable for controlling the following phytopathogenic fungi: Erysiphe graminis (powdery mildew) in cereals, Erysiphe cichoracearum and Sphaerotheca fuliginea in cucurbits, Podosphaera leucotricha in apples, Uncinula necator in grapevines, Puccinia species in cereals, Rhizoctonia species in cotton, rice and lawns, Ustilago species in cereals and sugar cane, Venturia inaequalis (scab) in apples, Helminthosporium species in cereals, Septoria nodorum in wheat, Botrytis cinera [sic] (gray mold) in strawberries, vegetables, ornamentals and grapevines, Cercospora arachidicola in groundnuts, 30 Pseudocercosporella herpotrichoides in wheat and barley, Pyricularia oryzae in rice, Phytophthora infestans in potatoes and tomatoes, Plasmopara viticola in grapevines, Pseudoperonospora species in hops and cucumbers, Alternaria species in vegetables and fruit, Mycosphaerella species in 35 bananas and Fusarium and Verticillium species.

40 The compounds II to V are commercially available as fungicides.

45 When preparing the mixtures, it is preferred to employ the pure active ingredients I and II to V, with which further active ingredients against harmful fungi or other pests, such as

insects, arachnids or nematodes, or else herbicidal or growth-regulating active ingredients or fertilizers can be admixed.

5 The mixtures of the compounds I and at least one compound II to V can be applied simultaneously, that is joined or separately, and have outstanding action against a wide range of phytopathogenic fungi, in particular from the classes of the Ascomycetes, Basidiomycetes, Phycomycetes and Deuteromycetes. Some of them act 10 systematically and are therefore also suitable for use as folio and soil-acting fungicides.

They are especially important for controlling a large number of fungi in a variety of crop plants, such as cotton, vegetable 15 species (for example cucumbers, beans, tomatoes, potatoes and cucurbits), barley, grass, oats, bananas, coffee, maize, fruit species, rice, rye, soya, grapevine, wheat, ornamentals, sugar cane, and a variety of seeds.

20 They are particularly suitable for controlling the following phytopathogenic fungi: *Erysiphe graminis* (powdery mildew) in cereals, *Erysiphe cichoracearum* and *Sphaerotheca fuliginea* in cucurbits, *Podosphaera leucotricha* in apples, *Uncinula necator* in 25 grapevines, *Puccinia* species in cereals, *Rhizoctonia* species in cotton, rice and lawns, *Ustilago* species in cereals and sugar cane, *Venturia inaequalis* (scab) in apples, *Helminthosporium* species in cereals and rice, *Septoria nodorum* in wheat, *Botrytis cinera* [sic] (gray mold) in strawberries, vegetables, ornamentals 30 and grapevines, *Cercospora arachidicola* in groundnuts, *Pseudocercospora herpotrichoides* in wheat and barley, *Pyricularia oryzae* in rice and lawns, *Phytophthora infestans* in potatoes and tomatoes, *Plasmopara viticola* in grapevines, *Pseudoperonospora* species in hops and cucumbers, *Alternaria* 35 species in vegetables and fruit, *Mycosphaerella* species in bananas and *Fusarium* and *Verticillium* species.

The mixtures according to the invention are particularly preferably utilizable for controlling *Pyricularia oryzae*.

40 The compounds I and at least one of the compounds II to V can be applied simultaneously, either together or separately, or in succession, the sequence, in the case of separate application, generally not having any effect on the control results.

45 Depending on the nature of the desired effect, the application rates of the mixtures according to the invention are, in

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particular in agricultural crops, from 0.01 to 8 kg/ha, preferably from 0.1 to 5 kg/ha, in particular from 0.5 to 3.0 kg/ha.

5 In the case of the compounds I, the application rates are from 0.01 to 2.5 kg/ha, preferably from 0.05 to 2.5 kg/ha, in particular from 0.1 to 1.0 kg/ha.

10 Correspondingly, in the case of the compounds II to V, the application rates are from 0.001 to 5 kg/ha, preferably from 0.005 to 2 kg/ha, in particular from 0.01 to 1.0 kg/ha.

15 For seed treatment, the application rates of the mixture are generally from 0.001 to 250 g/kg of seed, preferably 0.01 to 100 g/kg, in particular 0.01 to 50 g/kg.

20 If phytopathogenic harmful fungi are to be controlled, the separate or joint application of the compounds I and at least one of the compounds II to V is effected by spraying or dusting the seeds, the plants or the soils before or after sowing the plants, or before or after plant emergence.

25 The fungicidal synergistic mixtures according to the invention can be formulated for example in the form of ready-to-spray solutions, powders and suspensions or in the form of highly concentrated aqueous, oily or other suspensions, dispersions, emulsions, oil dispersions, pastes, dusts, materials for broadcasting or granules, and applied by spraying, atomizing, 30 dusting, broadcasting or watering. The use form depends on the intended purpose; in any case, it should ensure as fine and uniform as possible a distribution of the mixture according to the invention.

35 The formulations are prepared in a known manner, for example by expanding the active ingredient with solvents and/or carriers, if desired by use of emulsifiers and dispersants. If the diluent used is water, it is also possible to use other organic solvents as auxiliary solvents. Suitable auxiliaries are essentially:

40 solvents, such as aromatics (for example xylene), chlorinated aromatics (for example chlorobenzenes), paraffins (for example mineral oil fractions), alcohols (for example methanol, butanol), ketones (for example cyclohexanone), amines (for example ethanolamine, dimethylformamide) and water; carriers, such as 45 natural ground minerals (for example kaolins, clays, talc, chalk) and ground synthetic minerals (for example finely divided silica, silicates); emulsifiers, such as nonionic and anionic emulsifiers

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(for example polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates), and dispersants, such as ligninsulfite waste liquors and methylcellulose.

5 Suitable surfactants are the alkali metal salts, alkaline earth metal salts and ammonium salts of aromatic sulfonic acids, e.g. ligno-, phenol-, naphthalene- and dibutylnaphthalenesulfonic acid, and of fatty acids, alkyl- and alkylarylsulfonates, alkyl, lauryl ethers and fatty alcohol sulfates, and salts of sulfated 10 hexa-, hepta- and octadecanols, or of fatty alcohol glycol ethers, condensates of sulfonated naphthalene and its derivatives with formaldehyde, condensates of naphthalene or of the naphthalenesulfonic acids with phenol and formaldehyde, polyoxyethylene octylphenol ether, ethoxylated isoctyl-, octyl- 15 or nonylphenol, alkylphenol polyglycol ethers, tributylphenyl polyglycol ethers, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers or polyoxypropylene [sic], lauryl alcohol polyglycol ether acetate, sorbitol esters, 20 lignosulfite waste liquors or methylcellulose.

Powders, materials for broadcasting and dusts can be prepared by mixing or jointly grinding the compounds I and at least one of the compounds II to V or the mixture of the compounds I and at 25 least one of the compounds II to V with a solid carrier.

Granules (eg. coated granules, impregnated granules or homogeneous granules) are usually prepared by binding the active 30 ingredient, or active ingredients, to a solid carrier.

Fillers or solid carriers are, for example, mineral earths, such as silica gel, silicic acids, silica gels [sic], silicates, talc, kaolin, limestone, lime, chalk, bole, loess, clay, dolomite, 35 diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, and fertilizers, such as ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders or other 40 solid carriers.

The formulations generally comprise 0.1 to 95% by weight, preferably 0.5 to 90% by weight, of one of the compounds I and at least one of the compounds II to V or of the mixture of the 45 compounds I and at least one of the compounds II to V. The active ingredients are employed in a purity of from 90% to 100%.

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preferably 95% to 100% (according to NMR or HPLC spectrum [sic]).

The corresponding formulations are applied by treating the harmful fungi, their habitat or the plants, seeds, soils, areas, 5 materials or spaces to be kept free from them with a fungicidally effective amount of the mixture, or of the compounds I and at least one of the compounds II to V in the case of separate application.

10 Application can be effected before or after infection by the harmful fungi.

Examples of such preparations comprising the active ingredients 15 are:

I. A solution of 90 parts by weight of the active ingredients and 10 parts by weight of N-methylpyrrolidone; this solution is suitable for use in the form of microdrops;

20 II. A mixture of 20 parts by weight of the active ingredients, 80 parts by weight of xylene, 10 parts by weight of the adduct of 8 to 10 mol of ethylene oxide and 1 mol of oleic acid N-monoethanolamide, 5 parts by weight of the calcium salt of dodecylbenzenesulfonate, 5 parts by weight of the 25 adduct of 40 mol of ethylene oxide and 1 mol of castor oil; a dispersion is obtained by finely distributing the solution in water;

III. An aqueous dispersion of 20 parts by weight of the active 30 ingredients, 40 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 20 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil;

IV. An aqueous dispersion of 20 parts by weight of the active 35 ingredients, 25 parts by weight of cyclohexanol, 65 parts by weight of a mineral oil fraction of boiling point 210 to 280°C, and 10 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil;

V. A mixture, ground in a hammer mill, of 80 parts by weight 40 of the active ingredients, 3 parts by weight of the sodium salt of diisobutynaphthalene-1-sulfonic acid, 10 parts by weight of the sodium salt of a lignosulfonic acid from a sulfite waste liquor and 7 parts by weight of pulverulent silica gel; a spray mixture is obtained by finely distributing the mixture in water;

45 VI. An intimate mixture of 3 parts by weight of the active ingredients and 97 parts by weight of finely divided

kaolin; this dust comprises 3% by weight of active ingredient;

VII. An intimate mixture of 30 parts by weight of the active ingredients, 92 parts by weight of pulverulent silica gel and 8 parts by weight of paraffin oil which had been sprayed onto the surface of this silica gel; this formulation imparts good adhesion to the active ingredient;

VIII. A stable aqueous dispersion of 40 parts by weight of the active ingredients, 10 parts by weight of the sodium salt of a phenolsulfonic acid/urea/formaldehyde condensate, 2 parts by weight of silica gel and 48 parts by weight of water; this dispersion may be diluted further;

IX. A stable oily dispersion of 20 parts by weight of the active ingredients, 2 parts by weight of the calcium salt of dodecylbenzenesulfonic acid, 8 parts by weight of fatty alcohol polyglycol ether, 20 parts by weight of the sodium salt of a phenolsulfonic acid/urea/formaldehyde condensate and 88 parts by weight of a paraffinic mineral oil.

20 The synergistic activity of the mixtures according to the invention can be demonstrated by the following experiments:

25 The active ingredients, separately or together, are formulated as a 10% emulsion in a mixture of 63% by weight of cyclohexanone and 27% by weight of emulsifier, and correspondingly diluted with water to the desired concentration.

30 Evaluation is carried out by determining the infected leaf areas in percent. These percentages are converted into efficacies. The efficacy ( $W$ ) is calculated as follows using Abbot's formula:

$$W = (1 - \alpha) \cdot 100/\beta$$

35  $\alpha$  corresponds to the fungal infection of the treated plants in % and

$\beta$  corresponds to the fungal infection of the untreated (control) plants in %

40 An efficacy of 0 means that the infection level of the treated plants corresponds to that of the untreated control plants; an efficacy of 100 means that the treated plants were not infected.

45 The expected efficacies of the mixtures of the active ingredients were determined using Colby's formula [R.S. Colby, Weeds 15,

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20-22 (1967)] and compared with the observed efficacies.

Colby's formula:  $E = x + y - x \cdot y / 100$

5      E      is the expected efficacy, expressed in % of the untreated control, when using the mixture of the active ingredients A and B at the concentrations a and b

10     x      is the efficacy, expressed in % of the untreated control, when using active ingredient A at the concentration a

15     y      is the efficacy, expressed in % of the untreated control, when using active ingredient B at the concentration b

15      Use Example 1 - Activity against *Pyricularia oryzae* (protective)

15      Leaves of potted rice seedlings cv. "Tai-Nong 67" were sprayed to runoff point with an aqueous preparation of active ingredient which had been prepared from a stock solution comprising 10% of active ingredient, 63% of cyclohexanone and 27% of emulsifier.

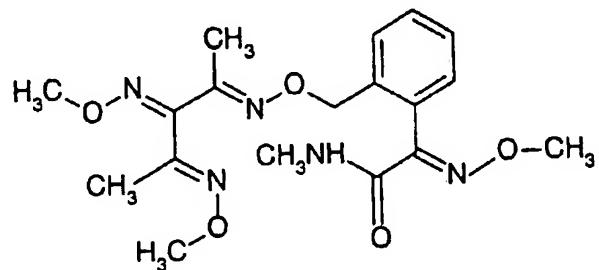
20      The following day, the plants were inoculated with an aqueous spore suspension of *Pyricularia oryzae*. The test plants were subsequently placed in climatized chambers at 22-24°C and 95-99% relative atmospheric humidity for 6 days. The extent of the development of the infection on the leaves was then determined

25      visually.

30      The visually determined values for the percentage of diseased leaf areas were converted into efficacies as percentage of the untreated control. An efficacy of 0 means the same disease level as in the untreated control, an efficacy of 100 means 0% disease. The expected efficacies for active ingredient combinations were determined using Colby's formula (Colby, S.R. "Calculating synergistic and antagonistic responses of herbicide combinations", Weeds, 15, pp. 20-22, 1967) and compared with the observed

35      efficacies.

The following compound I' was employed as component a):



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The results of the experiments are shown in Tables 1 and 2 below:

Table 1:

Ex.	Active ingredient	Conc. in ppm	Efficacy in % of the untreated control
1C	without	(100% disease)	0
2C	Compound I'	2.0	20
		0.5	0
3C	Compound II (common name: azoxystrobine)	0.5	20
4C	Compound III (common name: kresoxim-methyl)	2.0	0
		0.5	0

Table 2:

Ex.	Mixture according to the invention (conc. in ppm)	Observed efficacy	Calculated efficacy*
5	0.5 ppm I + 0.5 ppm II	40	20
6	2 ppm I + 2 ppm III	80	20
7	0.5 ppm I + 0.5 ppm III	20	0

\* calculated using Colby's formula

The test results show that for all mixing ratios the observed efficacy is higher than the efficacy which had been calculated beforehand using Colby's formula.

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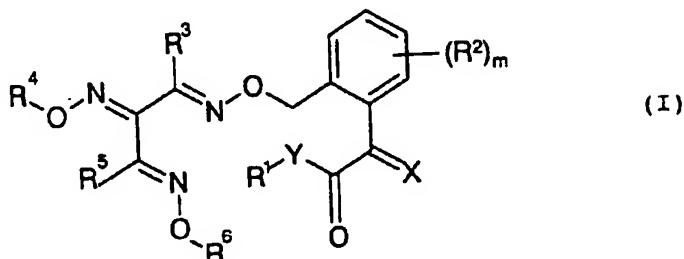
We claim:

5 I. A mixture for crop protection, comprising as active components

a) phenylacetic acid derivatives of the formula I

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in which the substituents and the index have the following meaning:

x is  $\text{NOCH}_3$ ,  $\text{CHOCH}_3$ ,  $\text{CHCH}_3$ ;

25

y is O, NR;

20  $\text{R}^1$ ,  $\text{R}$  independently of one another are each hydrogen and  $\text{C}_1\text{-C}_4$ -alkyl;

30

$\text{R}^2$  is cyano, nitro, trifluoromethyl, halogen,  $\text{C}_1\text{-C}_4$ -alkyl and  $\text{C}_1\text{-C}_4$ -alkoxy;

35

m is 0, 1 or 2, where the radicals  $\text{R}^2$  may be different if m is 2;

30  $\text{R}^3$  is hydrogen, cyano,  $\text{C}_1\text{-C}_4$ -alkyl,  $\text{C}_1\text{-C}_4$ -haloalkyl,  $\text{C}_3\text{-C}_6$ -cycloalkyl;

40

$\text{R}^4$ ,  $\text{R}^6$  independently of one another are each hydrogen, are  $\text{C}_1\text{-C}_{10}$ -alkyl,  $\text{C}_3\text{-C}_6$ -cycloalkyl,  $\text{C}_2\text{-C}_{10}$ -alkenyl,  $\text{C}_2\text{-C}_{10}$ -alkynyl,  $\text{C}_1\text{-C}_{10}$ -alkylcarbonyl,  $\text{C}_2\text{-C}_{10}$ -alkenylcarbonyl,  $\text{C}_3\text{-C}_{10}$ -alkynylcarbonyl or  $\text{C}_1\text{-C}_{10}$ -alkylsulfonyl, where these radicals may be partially or fully halogenated or may carry one to

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three of the following groups: cyano, nitro,  
 hydroxyl, mercapto, amino, carboxyl,  
 aminocarbonyl, aminothiocarbonyl, halogen,  
 C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-haloalkyl, C<sub>1</sub>-C<sub>6</sub>-alkylsulfonyl,  
 C<sub>1</sub>-C<sub>6</sub>-alkylsulfoxyl, C<sub>1</sub>-C<sub>6</sub>-alkoxy, C<sub>1</sub>-C<sub>6</sub>-haloalkoxy,  
 C<sub>1</sub>-C<sub>6</sub>-alkyloxycarbonyl, C<sub>1</sub>-C<sub>6</sub>-alkylthio,  
 C<sub>1</sub>-C<sub>6</sub>-alkylamino, di-C<sub>1</sub>-C<sub>6</sub>-alkylamino,

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are C<sub>1</sub>-C<sub>6</sub>-alkylaminocarbonyl,  
 10 di-C<sub>1</sub>-C<sub>6</sub>-alkylaminocarbonyl,  
 C<sub>1</sub>-C<sub>6</sub>-alkylaminothiocarbonyl,  
 di-C<sub>1</sub>-C<sub>6</sub>-alkylaminothiocarbonyl, C<sub>2</sub>-C<sub>6</sub>-alkenyl,  
 C<sub>2</sub>-C<sub>6</sub>-alkenyloxy, C<sub>3</sub>-C<sub>6</sub>-cycloalkyl,  
 C<sub>3</sub>-C<sub>6</sub>-cycloalkyloxy, heterocyclyl, heterocyclyloxy,  
 15 benzyl, benzyloxy, aryl, aryloxy, arylthio,  
 hetaryl, hetaryloxy and hetarylthio, where the  
 cyclic groups for their part may be partially or  
 fully halogenated or may carry one to three of the  
 following groups: cyano, nitro, hydroxyl,  
 20 mercapto, amino, carboxyl, aminocarbonyl,  
 aminothiocarbonyl, halogen, C<sub>1</sub>-C<sub>6</sub>-alkyl,  
 C<sub>1</sub>-C<sub>6</sub>-haloalkyl, C<sub>1</sub>-C<sub>6</sub>-alkylsulfonyl,  
 C<sub>1</sub>-C<sub>6</sub>-alkylsulfoxyl, C<sub>3</sub>-C<sub>6</sub>-cycloalkyl, C<sub>1</sub>-C<sub>6</sub>-alkoxy,  
 C<sub>1</sub>-C<sub>6</sub>-haloalkoxy, C<sub>1</sub>-C<sub>6</sub>-alkyloxycarbonyl,  
 25 C<sub>1</sub>-C<sub>6</sub>-alkylthio, C<sub>1</sub>-C<sub>6</sub>-alkylamino,  
 di-C<sub>1</sub>-C<sub>6</sub>-alkylamino, C<sub>1</sub>-C<sub>6</sub>-alkylaminocarbonyl,  
 di-C<sub>1</sub>-C<sub>6</sub>-alkylaminocarbonyl,  
 C<sub>1</sub>-C<sub>6</sub>-alkylaminothiocarbonyl,  
 di-C<sub>1</sub>-C<sub>6</sub>-alkylaminothiocarbonyl, C<sub>2</sub>-C<sub>6</sub>-alkenyl,  
 30 C<sub>2</sub>-C<sub>6</sub>-alkenyloxy, benzyl, benzyloxy, aryl, aryloxy,  
 arylthio, hetaryl, hetaryloxy, hetarylthio or  
 C(=NOR<sup>7</sup>)-A<sub>n</sub>-R<sup>8</sup>;

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are aryl, arylcarbonyl, arylsulfonyl, hetaryl, he-  
 tarylcarbonyl or hetaryl sulfonyl, where these ra-  
 diicals may be partially or fully halogenated or  
 may carry one to three of the following groups:  
 cyano, nitro, hydroxyl, mercapto, amino, carboxyl,  
 aminocarbonyl, aminothiocarbonyl, halogen,  
 C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-haloalkyl, C<sub>1</sub>-C<sub>6</sub>-alkylcarbonyl,  
 C<sub>1</sub>-C<sub>6</sub>-alkylsulfonyl, C<sub>1</sub>-C<sub>6</sub>-alkylsulfoxyl,  
 C<sub>3</sub>-C<sub>6</sub>-cycloalkyl, C<sub>1</sub>-C<sub>6</sub>-alkoxy, C<sub>1</sub>-C<sub>6</sub>-haloalkoxy,  
 C<sub>1</sub>-C<sub>6</sub>-alkyloxycarbonyl, C<sub>1</sub>-C<sub>6</sub>-alkylthio,  
 C<sub>1</sub>-C<sub>6</sub>-alkylamino, di-C<sub>1</sub>-C<sub>6</sub>-alkylamino,  
 C<sub>1</sub>-C<sub>6</sub>-alkylaminocarbonyl,  
 di-C<sub>1</sub>-C<sub>6</sub>-alkylaminocarbonyl,  
 C<sub>1</sub>-C<sub>6</sub>-alkylaminothiocarbonyl,

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di-C<sub>1</sub>-C<sub>6</sub>-alkylaminothiocarbonyl, C<sub>2</sub>-C<sub>6</sub>-alkenyl, C<sub>2</sub>-C<sub>6</sub>-alkenyloxy, benzyl, benzyloxy, aryl, aryloxy, hetaryl, hetaryloxy or C(=NOR<sup>7</sup>)-A<sub>n</sub>-R<sup>8</sup>;

5 R<sup>5</sup> is hydrogen,

is C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>2</sub>-C<sub>6</sub>-alkenyl, C<sub>2</sub>-C<sub>6</sub>-alkynyl, where the hydrocarbon radicals of these groups may be partially or fully halogenated or may carry one to three of the following radicals: cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocarbonyl, halogen, C<sub>1</sub>-C<sub>6</sub>-alkylaminocarbonyl, di-C<sub>1</sub>-C<sub>6</sub>-alkylaminocarbonyl, C<sub>1</sub>-C<sub>6</sub>-alkylaminothiocarbonyl, di-C<sub>1</sub>-C<sub>6</sub>-alkylaminothiocarbonyl, C<sub>1</sub>-C<sub>6</sub>-alkylsulfonyl, C<sub>1</sub>-C<sub>6</sub>-alkylsulfoxyl, C<sub>1</sub>-C<sub>6</sub>-alkoxy, C<sub>1</sub>-C<sub>6</sub>-haloalkoxy, C<sub>1</sub>-C<sub>6</sub>-alkoxycarbonyl, C<sub>1</sub>-C<sub>6</sub>-alkylthio, C<sub>1</sub>-C<sub>6</sub>-alkylamino, di-C<sub>1</sub>-C<sub>6</sub>-alkylamino, C<sub>2</sub>-C<sub>6</sub>-alkenyloxy, C<sub>3</sub>-C<sub>6</sub>-cycloalkyl, C<sub>3</sub>-C<sub>6</sub>-cycloalkyloxy, heterocyclyl, heterocyclxyloxy, aryl, aryloxy, aryl-C<sub>1</sub>-C<sub>4</sub>-alkoxy, arylthio, aryl-C<sub>1</sub>-C<sub>4</sub>-alkylthio, hetaryl, hetaryloxy, hetaryl-C<sub>1</sub>-C<sub>4</sub>-alkoxy, hetarylthio, hetaryl-C<sub>1</sub>-C<sub>4</sub>-alkylthio, where the cyclic radicals for their part may be partially or fully halogenated and/or may carry one to three of the following groups: cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocarbonyl, C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-haloalkyl, C<sub>1</sub>-C<sub>6</sub>-alkylsulfonyl, C<sub>1</sub>-C<sub>6</sub>-alkylsulfoxyl, C<sub>3</sub>C<sub>6</sub>-cycloalkyl [sic], C<sub>1</sub>-C<sub>6</sub>-alkoxy, C<sub>1</sub>-C<sub>6</sub>-haloalkoxy, C<sub>1</sub>-C<sub>6</sub>-alkoxycarbonyl, C<sub>1</sub>-C<sub>6</sub>-alkylthio, C<sub>1</sub>-C<sub>6</sub>-alkylamino, di-C<sub>1</sub>-C<sub>6</sub>-alkylamino, C<sub>1</sub>-C<sub>6</sub>-alkylaminocarbonyl, di-C<sub>1</sub>-C<sub>6</sub>-alkylamino-carbonyl, C<sub>1</sub>-C<sub>6</sub>-alkylaminothiocarbonyl, di-C<sub>1</sub>-C<sub>6</sub>-alkylaminothiocarbonyl, C<sub>2</sub>-C<sub>6</sub>-alkenyl, C<sub>2</sub>-C<sub>6</sub>-alkenyloxy, benzyl, benzyloxy, aryl, aryloxy, arylthio, hetaryl, hetaryloxy, hetarylthio and C(=NOR<sup>7</sup>)-A<sub>n</sub>-R<sup>8</sup>;

45 is C<sub>3</sub>-C<sub>6</sub>-cycloalkyl, C<sub>3</sub>-C<sub>6</sub>-cycloalkenyl, heterocyclyl, aryl, hetaryl, where the cyclic radicals may be partially or fully halogenated or

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may carry one to three of the following groups:  
 cyano, nitro, hydroxyl, mercapto, amino, carboxyl,  
 aminocarbonyl, aminothiocarbonyl, halogen,  
 5 C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-haloalkyl, C<sub>1</sub>-C<sub>6</sub>-alkylsulfonyl,  
 C<sub>1</sub>-C<sub>6</sub>-alkylsulfoxyl, C<sub>3</sub>-C<sub>6</sub>-cycloalkyl, C<sub>1</sub>-C<sub>6</sub>-alkoxy,  
 C<sub>1</sub>-C<sub>6</sub>-haloalkoxy, C<sub>1</sub>-C<sub>6</sub>-alkoxycarbonyl,  
 C<sub>1</sub>-C<sub>6</sub>-alkylthio, C<sub>1</sub>-C<sub>6</sub>-alkylamino,  
 10 di-C<sub>1</sub>-C<sub>6</sub>-alkylamino, C<sub>1</sub>-C<sub>6</sub>-alkylaminocarbonyl,  
 di-C<sub>1</sub>-C<sub>6</sub>-alkylaminocarbonyl,  
 C<sub>1</sub>-C<sub>6</sub>-alkylaminothiocarbonyl,  
 di-C<sub>1</sub>-C<sub>6</sub>-alkylaminothiocarbonyl, C<sub>2</sub>-C<sub>6</sub>-alkenyl,  
 C<sub>2</sub>-C<sub>6</sub>-alkenyloxy, benzyl, benzyloxy, aryl, aryloxy,  
 hetaryl and hetaryloxy;

15 where

A is oxygen, sulfur or nitrogen and where the nitrogen  
 carries hydrogen or C<sub>1</sub>-C<sub>6</sub>-alkyl;

20 n is 0 or 1;

R<sup>7</sup> is hydrogen or C<sub>1</sub>-C<sub>6</sub>-alkyl and

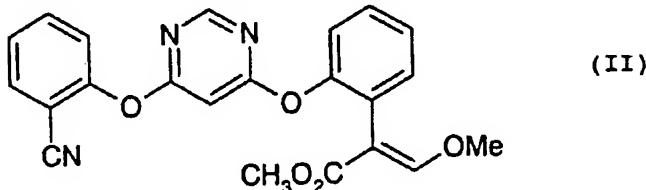
25 R<sup>8</sup> is hydrogen or C<sub>1</sub>-C<sub>6</sub>-alkyl,

and their salts,

30 and

b) at least one compound of the formulae II to V

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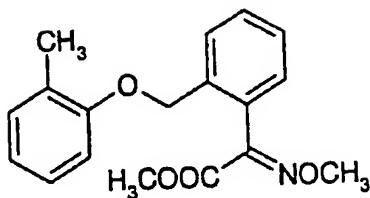


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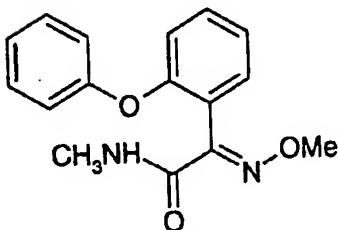
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(III)

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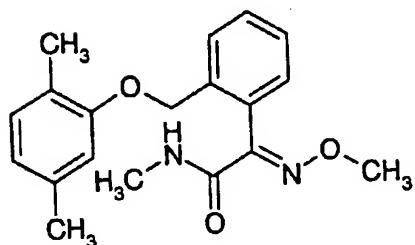
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(IV)

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(V)

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in a synergistically effective amount.

2. A fungicidal mixture as claimed in claim 1, which is conditioned in two parts, one part comprising the compound I in a solid or liquid carrier and the other part comprising at least one of the compounds II to V in a solid or liquid carrier.

3. A method for controlling harmful fungi, which comprises treating the fungi, their habitat, or the materials, plants, seeds, soils, areas or spaces to be protected against fungal attack with a fungicidal mixture as claimed in any of claims 1 to 2, where the application of the compound I and at least one of the compounds II to V may be carried out simultaneously, either together or separately, or in succession.

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4. A method as claimed in claim 3, wherein the harmful fungi, their habitat or the plants, seeds, soils, areas, materials or spaces to be kept free from them are treated with from 0.005 to 1 kg/ha of a compound I as set forth in claim 1.

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5. A method as claimed in claim 3, wherein the harmful fungi, their habitat or the plants, seeds, soils, areas, materials or spaces to be kept free from them are treated with from 0.01 to 1 kg/ha of at least one of the compounds II to V as  
10 set forth in claim 1.

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